

PHOTOLYSIS OF PHENYLBROMOPROPANES IN HEXANE.  
A FREE RADICAL REACTION INVOLVING A KINETIC PHENYL MIGRATION.

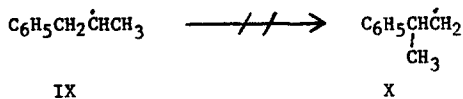
J.J. Dannenberg and K. Dill  
Hunter College of the City University of New York  
695 Park Avenue, New York, New York 10021

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The photolyses of 1-bromo-2-phenylpropane, I, and 2-bromo-1-phenylpropane, II, in hexane yield a variety of disproportionation products, III-VIII, in addition to higher molecular weight material (see table). The fact that disproportionation occurs, as well as, the fact that I forms chlorides when irradiated in the presence of  $\text{CCl}_4^1$  suggests that a free radical intermediate is formed. As in the case of the irradiation of I in the presence of  $\text{CCl}_4^1$ , the observed extent of rearrangement was much greater upon irradiation with 254 nm than with 313 nm.

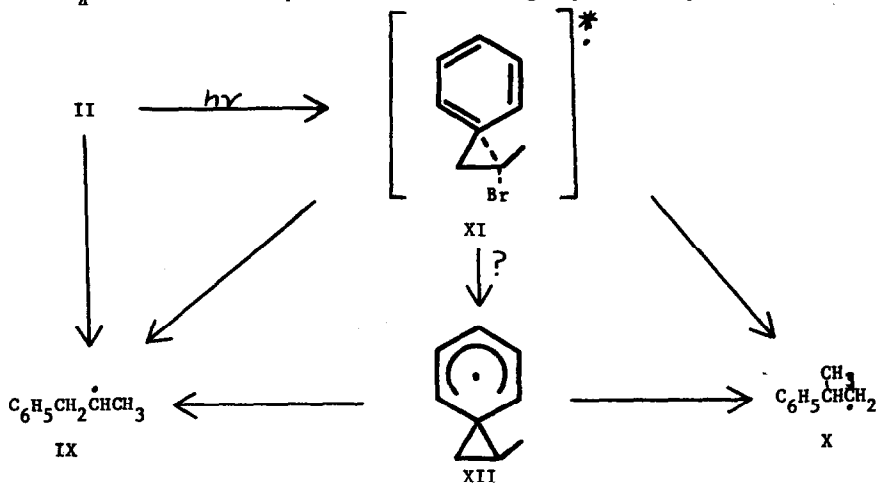
The irradiations were carried out in degassed quartz (254 nm) or Pyrex tubes (313 nm). The quantum yields were measured from sample tubes run to sufficiently low conversions (1-5%) that the formation of all products was proportional to irradiation time. The products were measured by g.l.c. and identified both by g.l.c. and by comparison of the Raman spectra of the eluted peaks collected by a new micro-sampling technique<sup>5</sup> with the spectra of authentic samples of III-VIII. The commercially available bromides I and II were distilled to 99+% purity (t.l.c.).

The formation of cumene, III, upon photolysis of II is of particular interest. Phenyl migrations in radical rearrangements have been known for some time. In particular, phenyl migrations in the neophyl radical<sup>2</sup> and in the 2-phenylethyl radical<sup>3,4</sup> have been extensively studied. Clearly, the rearrangement of the 1-phenyl-2-propyl radical, IX, to the 2-phenyl-1-propyl radical, X, is thermodynamically unfavorable. Only the thermodynamically favored reverse rearrangement (X $\rightarrow$ IX) has been reported.<sup>4</sup> Nevertheless, the formation of III from II



suggests the intermediacy of radical X. A possible mechanism for the formation of X involves

a bridged transition-state such as XI which could kinetically decay to a mixture of IX and X. This mechanism is analogous to that proposed for the photolysis of I in the presence of  $\text{CCl}_4$ <sup>1</sup>. The enhanced production of rearranged products upon irradiation of 254 nm



is explained by energy-transfer via the bridging transition state, XI, only when the excitation is initially localized in the phenyl group. Although this mechanism is somewhat different from those normally involved for energy-transfer, it has an analogy in the recently reported photorearrangement of 7-phenylhepta-2,4,diene<sup>6</sup>. The intermediacy of the bridged radical XII is of course suggested. The possible existence of phenyl-bridged radicals like XII has been intimated<sup>4</sup>, but never established. Although we favor the mechanism outlined above, one should note that the evidence does not exclude the possibility of reaction of a vibrationally "hot" intermediate, nor does it exclude the possibility that the multiplicity of the reactive intermediate is dependant upon the energy of the exciting light. This has been discussed previously.<sup>1</sup>

Recent attempts to generate a bridged phenylethyl radical in an e.s.r. cavity by photolyzing hydrocinnamoyl peroxide proved unsuccessful<sup>7</sup> as only the spectrum of the open phenylethyl radical was observed. However, the fact that 2.3-5.1% rearrangement was observed when  $\text{C}^{14}$ -labeled phenylethyl radical was produced by photolysis of 3-phenylpropionaldehyde<sup>3</sup> whereas 40% rearrangement was observed when the same radical was produced by treatment of 2-phenylethylbromide with magnesium and cobaltous bromide<sup>4</sup> suggests that the extent of rearrange-

		$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{CHCH}_3 \\ \text{III} \end{array} + \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{C}=\text{CH}_2 \\ \text{IV} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{V} \end{array} + \begin{array}{c} \text{trans} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VI} \end{array} + \begin{array}{c} \text{cis} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VII} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{VIII} \end{array}$	
$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{CHCH}_2\text{Br} \\ \text{I} \end{array}$	$\xrightarrow[\text{hexane}]{254 \text{ nm}}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_3 \\ \text{III} \end{array} + \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{C}=\text{CH}_2 \\ \text{IV} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{V} \end{array} + \begin{array}{c} \text{trans} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VI} \end{array} + \begin{array}{c} \text{cis} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VII} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{VIII} \end{array}$	<p>0.12    0.036    0.016    0.00068    — 0.0097 —</p>
$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{CHCH}_2\text{Br} \\ \text{I} \end{array}$	$\xrightarrow[\text{hexane}]{313 \text{ nm}}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_3 \\ \text{III} \end{array} + \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5\text{C}=\text{CH}_2 \\ \text{IV} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{V} \end{array} + \begin{array}{c} \text{trans} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VI} \end{array} + \begin{array}{c} \text{cis} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VII} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{VIII} \end{array}$	<p>0.0026    0.13    0.0014    0    0    0</p>
$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CHBrCH}_3 \\ \text{II} \end{array}$	$\xrightarrow[\text{hexane}]{254 \text{ nm}}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CHCH}_3 \\ \text{III} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{V} \end{array} + \begin{array}{c} \text{trans} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VI} \end{array} + \begin{array}{c} \text{cis} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VII} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{VIII} \end{array}$	<p>0.013    0    0.29    0.11    0.0061    0.090</p>
$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CHBrCH}_3 \\ \text{II} \end{array}$	$\xrightarrow[\text{hexane}]{313 \text{ nm}}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CHCH}_3 \\ \text{III} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{V} \end{array} + \begin{array}{c} \text{trans} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VI} \end{array} + \begin{array}{c} \text{cis} \\ \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 \\ \text{VII} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{VIII} \end{array}$	<p>0.0028    0    0.054    0.32    0.011    0</p>

TABLE  
Quantum Yields for Formation of Products III-VIII

ment, and therefore the extent to which the bridged radical might be formed, may depend upon the mechanism of radical generation. These observations could, of course, also be explained by a possible variation of radical lifetime with reaction conditions. Since the transition-state, XI, closely resembles the bridged radical XII, one might expect the proposed mechanism for the photolyses of I and II to be particularly favorable to the formation of XII. Studies, therefore, continue to further investigate the possible intermediacy of XII.

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#### References

1. J.J. Dannenberg, K. Dill and H.P. Waits, Chem. Comm., 1348 (1971).
2. See for example a) S. Winstein and F.H. Seubold, J. Am. Chem. Soc., 69, 2916 (1947);  
b) W.H. Urry and M.S. Kharasch, J. Am. Chem. Soc., 66, 1438 (1944).
3. L.H. Slaugh, J. Am. Chem. Soc., 81, 2262 (1959).
4. W.B. Smith and J.B. Anderson, J. Am. Chem. Soc., 82, 656 (1960).
5. B.J. Bulkin, K. Dill and J.J. Dannenberg, Analyt. Chem., 43, 974 (1971).
6. E.C. Sanford and G.S. Hammond, J. Am. Chem. Soc., 92, 3497 (1970).
7. J.K. Kochi and P.J. Krusic, J. Am. Chem. Soc., 91, 3941 (1969).